OPTIMIZATION OF COPPER OXIDE FILM BY DIP COATING TECHNIQUE FOR OXYGEN DETECTION

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This thesis is dedicated to

My father, Raship Bin Ab. Manas
My mother, Zaiton Binti Nasir
My sister, Nur Afiqah Binti Raship
My supervisor, Dr Mohd Zainizan Bin Sahdan
Staff MiNT-SRC, Pn. Faezahana Binti Mokhter
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ABSTRACT

Copper oxide (CuO) based gas sensor has been widely investigated due to its low-cost material, nontoxicity and abundant on earth. The CuO hierarchical structure is used to enhance the sensing performance of the gas sensor. This is because of its structure provides large surface area for the adsorption of gas into the sensing surface. However, most of the structure of CuO based gas sensors fabricated using various deposition techniques are particle structure. In this research, dip coating technique is proposed for the preparation of CuO hierarchical structure by optimized the annealing temperature, various pH of solutions and withdrawal speed of dip coating. The phase structure, morphology and surface roughness of CuO films were characterized by using X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and atomic force microscope (AFM), respectively. In addition, the thickness and electrical properties of CuO films were measured using surface profiler and four-point probe, respectively. Based on the results, 400 ^{o}C annealing temperature, pH 12.0 of CuO solution and 70 mm/min of withdrawal speed are the optimum parameters of CuO films for gas detection. The XRD results showed that these films have high crystal quality which crystallize along the (002) and (111) phase with preferential orientation along the c-axis of the CuO monoclinic structure. These films exhibit a uniform and homogeneous flower-like structure. The surface roughness of these films were 70.18 nm and the films thickness were found to be 0.76 µm. The electrical properties of these films show that they are conductive due to their lower resistivity which are 1.18 Ω.cm. Finally, these films were deposited at different withdrawal speed and their gas sensing ability towards oxygen gas were tested. As a result, CuO film at 70 mm/min of withdrawal speed exhibit sensitivity, response time and recovery time of 26.7 %, 2.381 s and 7.128 s, respectively. This research concludes that the CuO flower-like structure deposited by dip coating technique exhibit a good performance and works well as oxygen gas detection at room temperature.

ABSTRAK

Pengesan gas berasaskan kuprum oksida (CuO) telah dikaji secara meluas kerana kos bahan yang rendah, tiada toksik dan sumber yang banyak di bumi. Struktur hierarki CuO digunakan untuk meningkatkan prestasi pengesan gas. Ini kerana struktur hierarki mempunyai permukaan yang luas untuk penjerapan gas dengan permukaan filem. Walau bagaimanapun, kebanyakan struktur pengesan gas berasaskan CuO yang difabrikasi menggunakan pelbagai teknik pemendapan adalah struktur zarah. Dalam kajian ini, teknik penyalutan celup dicadangkan bagi penyediaan struktur hierarki CuO dengan pengoptimum suhu penyepulih-indapan, variasi larutan nilai pH dan kelajuan penarikan bagi penyalutan celup. Struktur fasa, morfologi dan kekasaran permukaan filem CuO dicirikan menggunakan alat difraksi sinar-X (XRD), mikroskop imbasan electron dengan percambahan medan (FESEM) dan mikroskop daya atom (AFM). Selain itu, ketebalan dan sifat elektrik filem diukur menggunakan pembukah permukaan dan instrumen prob empat titik. Hasilnya, 400 ^{o}C suhu penyepuhlih-indapan, nilai larutan CuO pada pH 12.0 dan kelajuan penarikan pada 70 mm/min adalah parameter optimum bagi filem CuO untuk pengesan gas. Hasil XRD menunjukkan filem ini mempunyai kualiti kristal yang baik serta mempunyai penumbuhan kristal sepanjang fasa (002) dan (111) dengan orientasi keutamaan di sepanjang paksi-c struktur monoklin CuO. Filem ini mempamerkan struktur seragam dan homogen. Kekasaran permukaan filem ini adalah 70.18 nm dan ketebalan filem adalah 0.76 µm. Ciri-ciri elektrik menunjukkan bahawa filem ini adalah jenis konduktif kerana rintangan yang rendah iaitu 1.18 Ω.cm. Akhirnya, filem ini direndapkan pada kelajuan penarikan yang berbeza dan pengujian keupayaan pengesan gas oksigen dijalankan. Hasilnya, filem CuO pada kelajuan pengeluaran 70 mm/min menunjukkan kepekaan, masa tindak balas dan pemulihan masa iaitu 26.7 %, 2.381 s dan 7.128 s. Kesimpulannya, filem CuO yang direndapkan menggunakan teknik penyalutan celup mempamerkan prestasi yang baik dan mampu mengesan gas oksigen pada suhu bilik.

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LIST OF SYMBOLS AND ABBREVIATIONS

2D	-	Two dimensional
3D	-	Three dimensional
^{o}	-	Degree
Θ	-	Bragg angle
%	-	Percentage
<	-	Less than
Ω	-	Ohm
λ	-	Wavelength
A	-	Ampere
Å	-	Angstrom
Ag	-	Silver
Ar	-	Argon
Au	-	Gold
AFM	-	Atomic force microscopy
ANSI	-	American national standard institute
AV	-	Aloe vera
ß	-	Beta
^{o}C	-	Temperature in celcius
cm	-	Centimeter
cm^2	-	Square centimeter
cm^3	-	Cubic centimeter
C_4Cl_2	-	Copper chloride
C_3H_8	-	Propane
$C_3H_6O_3$	-	Lactic acid
CBD	-	Chemical bath deposition
CdO	-	Cadmium oxide
CO	-	Carbon monoxide

CO_2	-	Carbon dioxide
Cr	-	Chromium
Cu	-	Copper
CuO	-	Copper (II) oxide
Cu_2O	-	Copper (I) oxide
$CuSO_4$	-	Copper sulfate
$CuSO_4.5H_2O$	-	Copper (II) sulfate pentahydrate
D	-	Crystallite size
DC	-	Direct current
DI	-	Distilled
e	-	Electron
eV	-	Electron volt
E_g	-	Band gap
EG	-	Ethylene glycol
FESEM	-	Field emission scanning electron microscope
FTO	-	Flourine doped tin oxide
FWHM	-	Full width at half maximum
g	-	Gram
g	-	Acceleration of gravity
Ge	-	Germanium
h	-	Coating thickness
h	-	Hour
hkl	-	Miller indices
H_2	-	Hydrogen
H_2O_2	-	Dihydrogen oxide
H_2S	-	Hydrogen sulfide
H_2SO_4	-	Sulfuric acid
HCHO	-	Formaldehyde
HF	-	Hydroflouric acid HMDA
	-	Hexamethylenediamine
HMT	-	Hexamethylene tetramine
HNO_3	-	Nitric acid
Hz	-	Hertz

ICSD	-	Inorganic crystal structure database
In_2O_2	-	Indium oxide
Ir	-	Iridium
JCPDS	-	Joint committee on powder diffraction standards
K	-	Scherrer's constant
k	-	Spring constant
kV	-	Kilo volt
$K_2Cr_2O_7$	-	Potassium dichromate
K	-	Kelvin
m	-	Meter
m_o	-	Hole effective mass
m^3	-	Cubic meter
min	-	Minute
ml	-	Milliliter
mm	-	Millimeter
mM	-	Millimolar
mTorr	-	Millitorr
M	-	Molar
MiNT-SRC	-	Microelectronic and Nanotechnology - Shamsuddin Research Centre
nm	-	Nanometer
N_2	-	Nitrogen
Na_2WO_4	-	Sodium tungstate
Na_2MoO_4	-	Sodium molybdate
NaOH	-	Sodium hydroxide
NH_3	-	Ammonia
NiO	-	Nickel oxide
NIOSH	-	National institute for occupational and health
NO_2	-	Nitrogen dioxide
O_2	-	Oxygen
p	-	Liquid density
p	-	Resistivity
pH	-	Potential of hydrogen

ppm	-	Parts per million
Pa	-	Pascal
Pd	-	Palladium
Pt	-	Platinum
PEG	-	Polyethylene glycol rpm
	-	Revolutions per minute
R_a	-	Resistance in the ambient air
R_g	-	Resistance of the sensor in target gas
RF	-	Radio frequency
Rh	-	Rhodium
s	-	Second
sccm	-	Standard cubic centimeters per minute
S	-	Sensitivity
Si	-	Silicon
SiO_2	-	Silicon dioxide
SDBS	-	Sodium dodecyl benzene sulphonate
SDS	-	Sodium dodecyl sulfate
SEM	-	Scanning electron microscope
$SnCl_4$	-	Tin chloride
SnO_2	-	Tin oxide
TiO_2	-	Titanium dioxide
µA	-	Microampere
µm	-	Micrometer
U	-	Withdrawal speed
U_o	-	Constant speed
v	-	Viscosity
V	-	Voltage
V_2O_5	-	Vanadium oxide
W	-	Watt
WO_3	-	Tungsten oxide
XRD	-	X-ray diffractometer
ZnO	-	Zinc oxide

CHAPTER 1

INTRODUCTION

This chapter introduced the importance and advantages of copper oxide (CuO) for the development of various applications including gas sensor and solar cell. In order to realize the aim and objectives of this study, a thorough background study on the structure of CuO films with different deposition techniques is disscussed in details. Based on the highlighted objectives, this chapter presents details of the study that is carried out and outcomes that are produced regarding optimization of CuO by dip coating techniques for oxygen gas detection.

1.1 Overview

In the past few decades, the metal oxide semiconductor has gained a huge interest due to their potential applications in a wide range of technological fields and also stability to control the material structure by different experimental technique. Earlier, research in the field has been devoted to bulk metal oxides such as zinc oxide (ZnO), tin oxide (SnO_2), titanium dioxide (TiO_2), cadmium oxide (CdO) and tungsten oxide (WO_3). Recently, the metal oxide semiconductor such as copper oxide (CuO), nickel oxide (NiO) and vanadium oxide (V_2O_5) have been attracting due to their unique chemical and physical properties [1]. Their properties are highly dependent on shapes, sizes, compositions, structure and morphology which are needed to be controlled. They are known as earth abundant, environmentally friendly, easy to synthesize and cost effective [2][3].

Among the semiconductor materials, CuO grabs the researcher interest and extensively studied due to its attractive properties and behaviour. CuO is one of the semiconductor materials categorized into transition metal oxide group and also known as tenorite. CuO is a p-type semiconductor with a band gap in the range of 1.2-1.5 eV [4][5]. Visually, CuO is commonly known to exhibit the colour tones. CuO usually appears as a dark grey or deep black. It also has monoclinic structure belong to space group 2/m with each Cu atom is coordinated by four O atoms in a square planar configuration. CuO has advantages of low cost material, high chemical stability and high electrical properties. CuO also has an excellent reactivity, easy to produce Cu oxidation, abundant on earth and nontoxicity. Due to such exclusive properties, CuO is used in various applications including gas sensor, solar cell, active catalyst, high efficiency thermal conducting material and magnetic recording media [6]. Recently, CuO have been receiving increased attention for their potential as sensing material due to growing number of publications. CuO have been studied as a sensitive layer for sensing a dangerous, inflammable and toxic gas due to several advantages, such as simplicity in the device structure, low cost for fabrication, robustness in practical applications, and adaptability to a wide variety of reductive or oxidative gasses. CuO also has been reported for nitrogen dioxide (NO_2) [4][7], hydrogen sulfide (H_2S) [8], carbon oxide (CO) [9], hydrogen (H_2) [10], methanol [11] and ethanol [12] sensors.

Recently, CuO were reviewed thoroughly in deposition technique for gas sensor application. The best method should be considered for producing the films. Several preparation methods have been used to fabricate the CuO films such as sputtering [11][13][14], electrodeposition [15][16], chemical vapor deposition [17] and sol-gel method [18][19][20]. Among these technique, dip coating technique has attracted much attention because it is a simple, reproducible and inexpensive technique. In addition, the easiness to control deposition parameters leads to the controlled properties suitable for each application. It is well known that films properties are very sensitive to the deposition parameters irrespective of deposition technique. The structural, morphological and electrical properties of the CuO layer give influence to the characteristics and performance of the CuO based gas sensor. Therefore, CuO films as a sensing layer prepared by dip coating technique may be a key to open the way to low cost, but high performing gas sensors.

1.2 Background study

Samarasekara *et al.* studied the sensitivity of CO_2 gas sensing by CuO deposited using reactive direct current (DC) sputtering [21]. They reported the sensitivity of CuO particles towards CO_2 gas is 5.1 with the detection time of 3 s. However, the recovery time at 200 ^{o}C is too long that is 25 min. Chapelle *et al.* studied gas sensing characteristics of CO_2 based on semiconducting spinel ferrite and CuO nanocomposites prepared by radio frequency (RF) sputtering [22]. The film showed particles structure with annealing treatment in air at 450 ^{o}C. It was found that the sensitivity of CuO particles is 1.9 and the response time is 9.5 h. However, the response time was long which is not practical for gas sensing application. Jundale *et al.* studied about CuO films which are deposited by spin coating technique for H_2S detection [23]. The CuO films were annealed at 700 ^{o}C exhibit particles structure. The result showed 25.2% sensing response for CuO particles at the gas concentration of 100 ppm at 200 ^{o}C of operating temperature.

Yang *et al.* synthesized p-type CuO particles using a microwave-assisted hydrothermal method [24]. The sensing response of CuO particles to ethanol was 9.8 at the operating temperature of 210 ^{o}C. The response time and the recovery time were within the range of 13–42 s and 17–51 s, respectively. Dhas *et al.* were fabricated CuO thin films by the method of spray pyrolysis with different molar concentration of 0.1M, 0.2M and 0.3M for ethanol sensor [25]. They verified that 0.3M film showed needle-like structure. They also observed that 0.3M film exhibited highest sensitivity of 33.66 and 36.84 for 100 and 200 ppm ethanol vapor.

Next, Nemade *et al.* reported on the various sensing properties of CuO towards CO_2 gas by spray pyrolysis of aqueous cupric nitrate solution [26]. The CuO nanoparticles showed good sensing response towards CO_2 gas which is 3.5 at 1000 ppm concentration. The detection time and recovery time of CuO was around 16 s and 20 s, respectively. Hung *et al.* prepared CuO flower-like structure using wet chemical-assisted hydrothermal method with different hydrothermal temperature [27]. The results revealed that the p-type semiconductor CuO flowers based sensors exhibit high sensitivity of 2.28 to ethanol vapor. The response time and recovery time were found to be 66 s and 197 s, respectively.

Wang *et al.* synthesized CuO nanoparticles using sol-gel method [28]. The sensing response of CuO nanoparticles to 0.1 ppm for acetone, methanol and ethanol

gas are 2.5, 1.9 and 2.7, respectively. The response/recovery time are 10 s/6 s, 11 s/6 s and 11 s/7 s, for acetone, methanol and ethanol gas, respectively. Most recently, Fazliana *et al.* investigated the influence of deposition time towards CuO based oxygen gas sensor fabricated by chemical bath deposition (CBD) technique [29]. Nanostructured CuO thin films were varied at 3 h, 5 h and 7 h. The surface of CuO films at 5 h deposition showed nanowhiskers structures. The CuO nanowhiskers structures have high response time towards O_2 gas at room temperature which is 180 s.

From this review, many researchers studied on CuO by various preparation methods which their aims are to find the best properties of the CuO film for gas sensor application. However, most of their structure and morphology were grown on CuO films are particle structure with lack performance of the gas sensor. Such hierarchical structure have high surface to volume ratio with aligned porous which provide large surface area for the adsorption of gas into the entire sensing surface. Furthermore, the dip coating technique has not been reported widely by the previous researchers. Thus, the research on dip coating technique will be presented in this thesis in order to get better properties of CuO films as well as hierarchical structure of CuO.

1.3 Problem Statement

Recently, a need to develop a low cost gas sensor with high sensitivity and fast response for detecting oxygen gas at low operating temperature. According to National Institute for Occupational and Health (NIOSH), low level of oxygen concentration give effects to human health and can cause death [30]. In order to improve the performance of the gas sensor, hierarchical structure of the sensing film such as flower-like structure is reported as a suitable structure for gas sensor application [31]. Previous researchers found that the hierarchical structure provides large surface area for the adsorption of gas into the entire sensing surface [32][33]. Thus, it will enhance the performance of the gas sensor.

Previously, CuO films have been fabricated using reactive sputtering, thermal evaporation, thermal oxidation, electrochemical and chemical deposition [34]. However, most of the researchers reported that CuO structure prepared with various deposition technique results in the formation of particle structure with long fabrication time and lack performance of the gas sensor. Aslani *et al.* fabricated CuO nanoparticles using a hydrothermal technique. The fabrication time was 24 h and the sample was heated at 150 ^{o}C [3]. Then, the sample was annealed in vacuum condition at 400 ^{o}C for 2 h. The response time and recovery time were 25 s and 150 s, respectively. Li *et al.* have deposited CuO particles by thermal decomposition. The film was deposited at 90 ^{o}C and annealed at 500 ^{o}C for 4 h in order to get CuO phase [4]. The response time and recovery time of CuO film were 24 s and 45 s, respectively. Since the conventional methods are using high temperature and longer deposition time, therefore dip coating technique was proposed to prepare the hierarchical structure of CuO for oxygen gas detection. Instead of using the expensive and sophisticated technique, a simple method is very convenient to produce uniform and fine hierarchical structure. Moreover, the dip coating technique is one of the promising methods that provide shorter fabrication time with low annealing temperature which can reduce the cost of film fabrication. Thus, CuO hierarchical structure deposited using dip coating technique is expected can improve the properties of CuO films as well enhance the sensing performance of oxygen, (O_2) gas sensor at room temperature.

1.4 Objectives of the study

The objectives of this study are:

i. To deposit CuO hierarchical structure using sol-gel dip coating technique.
ii. To optimize the structural, morphological and electrical properties of the CuO film by dip coating technique.
iii. To test the potential of CuO film for oxygen (O_2) gas sensor.

1.5 Scopes of the study

The scopes of this study are:

i. The deposition of CuO film using sol-gel dip coating technique.
ii. Copper (II) sulfate pentahydrate, deionized water, lactic acid and sodium hydroxide was used in solution preparation.

iii. Deposition of CuO films at 200 ^{o}C, 300 ^{o}C and 400 ^{o}C of annealing temperature.
iv. Deposition of CuO films at pH 12.0, pH 12.3 and pH 12.5 of pH value of CuO solution.
v. Deposition of CuO films at 70 mm/min, 110 mm/min and 150 mm/min of withdrawal speed.
vi. The phase structure, surface morphology, porosity, surface roughness, thickness and electrical properties of CuO films was characterized by using X-ray diffractometer (XRD), field emission scanning electron microscope (FESEM), atomic force microscopy (AFM), surface profiler and four point probe.
vii. The sensor response of CuO film for oxygen gas was determine by measuring the resistance changes using a high precision digital multimeter.
viii. The response time and recovery time was measure using Matlab (R2012a).

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